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**(54) POLYOLEFIN MICROPOROUS FILM AND METHOD FOR PREPARING THE SAME**

(57) It is an object of the present invention to provide a microporous polyolefin membrane, high in pin puncture strength, adequate in pore diameter and high in porosity, comprising (A) an ultra-high-molecular-weight polyolefin having a weight-average molecular weight of  $5 \times 10^5$  or more, or (B) a composition containing an ultra-high-molecular-weight polyolefin having a weight-average molecular weight of  $5 \times 10^5$  or more, and having a porosity of 30 to 95%, bubble point exceeding 980 KPa and pin puncture strength of 4,900 mN/25  $\mu$ m or more.

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## Description

## TECHNICAL FIELD

- 5 [0001] This invention relates to a microporous membrane comprising an ultra-high-molecular-weight polyolefin or composition containing an ultra-high-molecular-weight polyolefin, more particularly to a microporous polyolefin membrane for battery separators, and also relates to a method for producing the same.

## BACKGROUND OF THE INVENTION

- 10 [0002] Microporous polyolefin membranes are widely used in various applications such as battery separators (in particular, separators for lithium ion primary and secondary batteries and large-sized batteries for electric vehicles or the like), capacitor separators, various separation membranes (e.g., for water treatment, ultrafiltration, microfiltration and reverse osmosis), various filters, and moisture-permeable/waterproof clothes or base materials therefor, because  
15 they are insoluble in organic solvents, and resistant to electrolytes and electrode-active materials.

- [0003] One of the known methods for producing microporous polyolefin membranes is extraction process comprising the steps of mixing a polyolefin with an organic medium and inorganic powder (e.g., finely powdered silica), melting and molding the mixture, and extracting the organic solvent and inorganic powder. This method needs a process of extracting the inorganic powder, and permeability of the membrane produced depends largely on particle size of the  
20 inorganic powder used and is difficult to control.

- [0004] Recently, various processes have been proposed to produce high-strength, microporous membranes which contain an ultra-high-molecular-weight polyolefin. For example, Japanese Patent Application Laid-Open Nos. 60-242035, 61-195132, 61-195133, 63-39602, 63-273651, 3-64334 and 3-105851 disclose processes to produce microporous membranes by forming a gel-like sheet from a heated solution of a polyolefin composition containing an ultra-  
25 high-molecular-weight polyolefin dissolved in a solvent, stretching it while heating, and removing the solvent by extraction. These processes give the microporous polyolefin membranes characterized by a sharp pore size distribution and small pore size, which have been used for battery separators.

- [0005] Recently, lithium ion batteries have been increasingly required to have higher battery characteristics, safety and productivity. The functions these batteries are required to have include battery capacity at low temperature for the improved battery characteristics, and permeability of the lithium ions and a function of controlling effects of clogging for the recycling characteristics. In order to improve battery characteristics, it is generally essential to reduce energy loss by increasing separator permeability and decreasing ion migration resistance in a range that safety of the battery is securely kept. It should be noted that excessively increasing pore size helps accelerate formation of dendrite, possibly deteriorating safety of the battery. It is necessary, when the battery is subjected to a destructive test, the electrodes are  
30 securely kept apart from each other for safety reasons, even when the separator is deformed. Development of the separator having a high pin puncture strength, adequate pore diameter and high porosity (permeability) has been increasingly demanded.

- [0006] It is an object of the present invention to provide a microporous polyolefin membrane, high in pin puncture strength, adequate pore diameter and high porosity (permeability), and excellent in battery characteristics and high in  
40 safety when used for battery separators.

## DISCLOSURE OF THE INVENTION

- [0007] The inventors of the present invention have found, after having extensively studied to solve the above-described problems, that a microporous polyolefin membrane well-balanced between high pin puncture strength and porosity can be produced by biaxially stretching a gel-like formed product of solution comprising a specific content of an ultra-high-molecular-weight polyolefin or composition containing an ultra-high-molecular-weight polyolefin dissolved in a solvent under optimized stretching conditions (e.g., stretching ratio) and then heat-setting the stretched product also under optimized conditions, to reach the present invention.  
45

- 50 [0008] Thus, the present invention provides a microporous polyolefin membrane comprising (A) an ultra-high-molecular-weight polyolefin having a weight-average molecular weight of  $5 \times 10^5$  or more, or (B) a composition containing an ultra-high-molecular-weight polyolefin having a weight-average molecular weight of  $5 \times 10^5$  or more, and having a porosity of 30 to 95%, bubble point exceeding 980 KPa and pin puncture strength of 4900 mN/25  $\mu$ m or more.

- [0009] The present invention also provides a method for producing a microporous polyolefin membrane, which  
55 comprises the steps of (a) preparing a solution comprising 10 to 40 wt.% of (A) an ultra-high-molecular-weight polyolefin having a weight-average molecular weight of  $5 \times 10^5$  or more, or (B) a composition containing an ultra-high-molecular-weight polyolefin having a weight-average molecular weight of  $5 \times 10^5$  or more, and 90 to 60 wt.% of a solvent, (b) extruding the solution, (c) quenching the extruded solution to have a gel-like extrudate, (d) biaxially stretching the gel-

like extrudate at 110 to 120°C at a stretching ratio of 5 or more in both MD and TD directions, (e) removing the solvent and drying the extrudate, and (f) heat-setting the extrudate at 115 to 125°C.

## PREFERREED EMBODIMENTS OF THE INVENTION

**[0010]** The microporous polyolefin membrane of the present invention is described in more detail by constituent components, properties and method of production.

### 1. Polyolefin

**[0011]** The ultra-high-molecular-weight polyolefin (A) for the microporous polyolefin membrane of the present invention has a weight-average molecular weight of  $5 \times 10^5$  or more, preferably in a range from  $1 \times 10^6$  to  $15 \times 10^6$ . A polyolefin having a weight-average molecular weight less than  $5 \times 10^5$  is undesirable for the present invention, because of anticipated deterioration of membrane strength.

**[0012]** The composition (B) containing an ultra-high-molecular-weight polyolefin having a weight-average molecular weight of  $5 \times 10^5$  or more is not limited. One of the preferred examples of the composition (B) comprises an ultra-high-molecular-weight polyolefin (B-1) having a weight-average molecular weight of  $1 \times 10^6$  or more, preferably  $1.5 \times 10^6$  or more, more preferably  $1.5 \times 10^6$  to  $15 \times 10^6$  and a polyolefin (B-2) having a weight-average molecular weight of  $1 \times 10^4$  or more but less than  $1 \times 10^6$ , preferably  $1 \times 10^5$  or more but less than  $5 \times 10^5$ . It is necessary for the composition (B) to contain the ultra-high-molecular-weight polyolefin (B-1) at 1 wt.% or more. The composition containing the ultra-high-molecular-weight polyolefin (B-1) at less than 1 wt.% will not give the microporous membrane of sufficient strength, because the molecular chains of the polyolefin (B-1) are scarcely entwined with each other. When the polyolefin (B-2) has a weight-average molecular weight less than  $1 \times 10^4$ , it cannot give a desired microporous membrane, because it tends to be broken.

**[0013]** Examples of the above-described polyolefins include crystalline homopolymers, two-stage polymers or copolymers of ethylene, propylene, 1-butene, 4-methyl-pentene-1, 1-hexene, 1-octene, vinyl acetate, methyl methacrylate or styrene, or blends thereof. Preferable among them are polypropylene, polyethylene and compositions thereof. Polyethylenes may be of high density, low density or medium density. Of these, the preferable ones are the compositions comprising an ultra-high-molecular-weight polyolefin (B-1) having a weight-average molecular weight of  $1 \times 10^6$  or more and high-density polyethylene (B-2) having a weight-average molecular weight of  $1 \times 10^4$  or more but less than  $1 \times 10^6$ . Particularly preferable compositions are those comprising an ultra-high-molecular-weight polyolefin (B-1) having a weight-average molecular weight of  $1 \times 10^6$  or more and high-density polyethylene (B-2) having a weight-average molecular weight of  $1 \times 10^5$  or more but less than  $5 \times 10^5$ . It is most preferable that 100 wt. parts of the composition (B) comprises 20 to 60 wt. parts of a polyolefin (B-1) and 40 to 80 wt. parts of a high-density polyethylene (B-2).

**[0014]** Low-density polyethylene may be incorporated as the polyolefin which imparts a shut-down function to the membrane, to improve its characteristics for battery separators. The low-density polyethylene useful for the present invention includes linear low-density polyethylene (LLDPE) produced by the medium pressure method, low-density polyethylene (LDPE) produced by the high pressure method, and ethylene/ $\alpha$ -olefin copolymer produced in the presence of a single site catalyst.

**[0015]** The polypropylenes useful for the present invention include block and random copolymers, in addition to the homopolymer. The block and random copolymers may be incorporated with another type of  $\alpha$ -olefin other than propylene. One of the preferred  $\alpha$ -olefins is ethylene. Incorporation of polypropylene can improve melt-down temperature and as a result, characteristics of the membrane for battery separators can be improved.

**[0016]** The microporous polyolefin membrane of the present invention may be further incorporated with a low-molecular-weight polyethylene having a weight-average molecular weight of 1000 to 4000 as an optional component to improve its characteristics for battery separators. In such a case, its content is preferably kept at 20 wt.% or less, based on the whole polyolefin composition, because the polyolefin of insufficient weight-average molecular weight tends to cause breakdown of the microporous membrane, as described above.

**[0017]** The above-described polyolefin or polyolefin composition has a molecular weight distribution (weight-average molecular weight/number-average molecular weight) of 300 or less, preferably 5 to 50. The molecular weight distribution above 300 is undesirable, because the membrane comprising such a composition may suffer breakdown by the lower molecular weight components to lose its strength as a whole. When the polyolefin composition is used, the desirable molecular weight distribution can be obtained by adequately mixing an ultra-high-molecular-weight polyolefin having a weight-average molecular weight of  $1 \times 10^6$  or more and a polyolefin having a weight-average molecular weight of  $1 \times 10^5$  or more but less than  $5 \times 10^5$ . The composition may be produced by a multi-stage process or mixing two or more types of polyolefin, so long as it has the above molecular weight and molecular weight distribution.

**[0018]** The above-described polyolefin or polyolefin composition may be incorporated, if required, with various additives such as antioxidants, ultraviolet absorbers, antiblocking agents, pigments, dyes, inorganic fillers, etc., within

limits not harmful to the object of the present invention.

## 2. Microporous polyolefin membrane

### (1) Properties

**[0019]** The microporous polyolefin membrane of the present invention has the following properties:

#### (i) Porosity

**[0020]** The microporous polyolefin membrane of the present invention has a porosity of 30 to 95%, preferably 35 to 95%, more preferably 45 to 95%. Porosity beyond the above-described range is undesirable. At below 30%, the membrane may be insufficient in ion conductivity for battery separators, deteriorated in battery characteristics, e.g., battery capacity and cycle characteristics, especially at low temperature. At above 95%, on the other hand, strength of the membrane itself is insufficient.

#### (ii) Bubble point

**[0021]** The microporous polyolefin membrane of the present invention has a bubble point above 980 KPa, preferably above 1,470 KPa, more preferably above 14,700 KPa. Bubble point of 980 KPa or less is undesirable for a battery separator microporous polyolefin membrane, because such a membrane may have excessively large pores to accelerate formation of dendrite, possibly causing various troubles, e.g., voltage drop and self-discharge.

#### (iii) Pin puncture strength

**[0022]** The microporous polyolefin membrane of the present invention has a pin puncture strength of 4,900 mN/25  $\mu\text{m}$  or more, preferably 6,860 mN/25  $\mu\text{m}$  or more. Pin puncture strength below 4,900 mN/25  $\mu\text{m}$  is undesirable for a microporous polyolefin membrane for battery separators, because irregularities and/or burrs on the electrodes may press the separator to cause minute short circuits.

#### (iv) Tensile elongation

**[0023]** The microporous polyolefin membrane of the present invention has a tensile elongation of 300% or more. The membrane having such a tensile elongation is advantageous in that the battery separator thereof absorbs thermal stresses resulting from heat generated inside and hence is more difficult to break.

#### (v) Average pore diameter

**[0024]** The microporous polyolefin membrane of the present invention has pores preferably having an average diameter of 0.01 to 0.1  $\mu\text{m}$ , more preferably 0.01 to 0.05  $\mu\text{m}$ . At an average diameter below 0.01  $\mu\text{m}$ , the membrane may have an excessively low permeability. At above 0.1  $\mu\text{m}$ , on the other hand, the membrane tends to suffer voltage drop and self-discharge resulting from formation of dendrite, when it is used for a battery separator.

#### (vi) Tensile strength

**[0025]** The microporous polyolefin membrane of the present invention preferably has a tensile strength of 49,000 KPa or more both in the MD and TD directions, more preferably 80,000 KPa or more, still more preferably 127,400 KPa. The microporous polyolefin membrane having a tensile strength of 49,000 KPa or more will not be broken, when used for a battery separator, and hence is desirable.

**[0026]** The microporous polyolefin membrane having a pin puncture strength of 6,860 mN/25  $\mu\text{m}$  or more and tensile strength of 127,400 KPa/cm<sup>2</sup> or more can prevent minute short circuits resulting from irregularities and/or burrs on the electrodes, when used for a battery separator, even when it is as thin as 16  $\mu\text{m}$  or less.

#### (vii) Air permeability

**[0027]** The microporous polyolefin membrane of the present invention preferably has an air-permeability of 900 sec/100 cc or less, more preferably 800 sec/100 cc or less, still more preferably 100 to 800 sec/100 cc. Keeping air-permeability at 900 sec/100 cc or less for the microporous polyolefin membrane can improve its ion transmission capac-

ity and hence output characteristics, when it is used for a battery separator.

(viii) Resistance to pinholing

**[0028]** The microporous polyolefin membrane of the present invention is preferably highly resistant to pinholing. Resistance to pinholing is an index defined as changed air-permeability when the sample is pressed with a pin (diameter: 1 mm) at a load of 1000 g for 5 seconds. The microporous membrane is judged to be resistant to pinholing, when the tested sample loses less than 50% of its initial air permeability.

**[0029]** The microporous polyolefin membrane of the present invention, satisfying the above-described conditions, is high in elongation, permeability, and strength. In spite of its high bubble point, it is relatively small in average pore diameter at 0.01 to 0.1  $\mu\text{m}$ , high in porosity, sharp in pore size distribution, and conversely high in permeability. These properties, coupled with its high resistance to pinholing, make the microporous polyolefin membrane of the present invention suitable for, e.g., battery separators and liquid filters.

(2) Production of the microporous polyolefin membrane

**[0030]** The method for producing the microporous polyolefin membrane of the present invention comprises steps of (a) mixing a resin component of a polyolefin or polyolefin composition, incorporated, as required, with a polymer or the like which imparts a shut-down effect at low temperature to the membrane, with an organic liquid or solid, (b) melting, kneading and extruding the mixture, and (c) stretching, extracting, drying and heat-setting the extrudate. One of the preferred embodiments for producing the microporous polyolefin membrane of the present invention comprises preparing a solution of polyolefin or polyolefin composition by supplying it with a good solvent for the polyolefin, extruding the solution through a die into sheets, cooling the sheets to form the gel-like composition, stretching the gel-like composition under heating, and removing the residual solvent from the composition.

**[0031]** In the present invention, the solution of polyolefin or polyolefin composition as the stock is prepared by dissolving the polyolefin or polyolefin composition in a solvent while heating. Any solvent can be used, so long as it can sufficiently dissolve the polyolefin. Examples of the solvents include aliphatic or cyclic hydrocarbons such as nonane, decane, undecane, dodecane, paraffin oils, etc., and fractions of mineral oils having boiling points substantially equal to those of the above hydrocarbons. A nonvolatile solvent, e.g., paraffin oil, is preferable for forming the stable gel-like shape.

**[0032]** Dissolution of the polyolefin or polyolefin composition while heating is carried out by stirring its solution at a temperature at which it is completely dissolved in the solvent, or uniformly mixing the polyolefin or polyolefin composition and solvent with each other in an extruder. When the polyolefin or polyolefin composition is to be dissolved in the solvent with stirring, the dissolving temperature varies depending on the types of polymers and solvents used. It is in the range of 140 to 250°C in the case of polyethylene composition. It is preferable to effect the dissolution in an extruder, when a high-concentration solution of the polyolefin composition is used to produce a microporous membrane.

**[0033]** When the dissolution is to be effected in an extruder, the polyolefin or polyolefin composition is first charged in the extruder to be molten, at a temperature preferably 30 to 100°C above melting point of the polyolefin, although varying depending on type of the polyolefin used, where melting point is determined by DSC in accordance with JIS K 7211 (valid throughout this specification). For example, it is 160 to 230°C, preferably 170 to 200°C, in the case of polyethylene, and 190 to 270°C, preferably 190 to 250°C, in the case of polypropylene. Then, a liquid solvent is added to the molten polyolefin or polyolefin composition in the middle of the extruder.

**[0034]** The concentration of the polyolefin or polyolefin composition is 10 to 40 wt. % based on the total of the polyolefin or polyolefin composition and solvent, preferably 15 to 35 wt.%, more preferably 15 to 30 wt.%, or conversely the concentration of the solvent is 90 to 60 wt.%, preferably 85 to 65 wt.%, more preferably 85 to 70 wt.%. When the polyolefin or polyolefin composition concentration is less than 10 wt.% (or the solvent concentration is more than 90 wt.%), swelling and neck-in are likely to take place at the exit of a die in the process of forming sheets. Accordingly, it is difficult to keep good molding processability and self-supporting characteristics of the sheet produced. Another disadvantage is decreased productivity resulting from longer time required to remove the solvent. On the other hand, when the polyolefin or polyolefin composition concentration is more than 40 wt.% (or the solvent concentration is less than 60 wt.%), the sheet will suffer deteriorated molding processability. It is possible to control permeability of the membrane by changing the polyolefin or polyolefin composition concentration in the above range.

**[0035]** Next, the heated solution of the molten and kneaded polyolefin or polyolefin composition is extruded directly or by another extruder through a die or the like, in such a way to secure the final membrane thickness of 5 to 250  $\mu\text{m}$ .

**[0036]** Usually used as a die is a sheet die having a rectangular orifice, but a double-pipe hollow die, an inflation die, etc. may be used. When the sheet die is used, a die gap is usually 0.1 to 5mm, and heated at 140 to 250°C in the extrusion process.

**[0037]** The solution extruded through the die is formed into a gel-like sheet by quenching. It is cooled to 90°C or

below, preferably to 80 to 30°C, at a speed of at least 50°C/minute by cooling the die or gel-like sheet. As a method of cooling the gel-like sheet, direct contact with cooling air, cooling water or other cooling media, contact with a roll cooled by a coolant, etc. may be employed. Contact with a cooled roll is a preferable method.

[0038] The gel-like sheet is then biaxially stretched under heating by an ordinary method, such as a tenter, roll, calender method or a combination thereof at a given stretching ratio. It may be stretched in the machine and transmachine directions simultaneously or sequentially. The simultaneous stretching is more preferable.

[0039] The stretching temperature is 110 to 120°C, preferably 113 to 120°C, for producing a high-strength microporous polyolefin membrane, such as that of the present invention, from a composition of an ultra-high-molecular-weight polyethylene and high-density polyethylene.

[0040] The stretching ratio should be set at 5 or more for both MD and TD directions. A microporous polyolefin membrane may not have a sufficient pin puncture strength, when stretched at a stretching ratio below 5 in either direction.

[0041] The stretched sheet is then washed with a solvent to remove the residual solvent. Solvents used for this solvent-removing treatment may be volatile ones, including hydrocarbons such as pentane, hexane and heptane; chlorinated hydrocarbons such as methylene chloride and carbon tetrachloride; fluorinated hydrocarbons such as trifluoroethane; and ethers such as diethyl ether and dioxane. These solvents may be used individually or in combination, and their selection depends on the types of the nonvolatile solvents used to dissolve the polyolefin composition. Washing methods with the solvents include an extraction method with solvents in which the sheet is immersed, a method of spraying solvents or a combination thereof.

[0042] The washing of the stretched sheet with a solvent should be performed to such an extent that the content of the residual solvent is less than 1 wt.%. The stretched sheet is finally dried to remove the washing solvent by a heating method, an air-drying method, etc.

[0043] The dried sheet is heat-set at 115 to 125°C. Treating the sheet at a temperature in this range will give a porous, highly strong membrane having a high porosity of 45% or more. A microporous membrane having a pin puncture strength of 6,860 mN/25 µm or more and tensile strength of 127,400 KPa or more will result, when the sheet is heat-set at above 120°C but 125°C or lower.

[0044] The microporous membrane having the desired properties can be produced by the above-described procedure. It may be subjected, if necessary, to a hydrophilic treatment by plasma irradiation, impregnation with a surface active agent, surface grafting, etc. for surface modification.

#### EXAMPLES AND COMPARATIVE EXAMPLES.

[0045] The present invention is described in more detail by the following preferred embodiments, which by no means limit the present invention. The properties cited in the preferred embodiments were determined by the following test methods:

(1) Weight-average molecular weight and molecular weight distribution: Determined by gel permeation chromatography (GPC), where chromatograph: Waters' analyzer, column: Tosoh's GMH-6, solvent: o-dichlorobenzene, temperature: 135°C, and flow rate: 10 ml/min

(2) Membrane thickness: Determined by a stylus type thickness meter (Mitsutoyo Litematic)

(3) Air permeability: Measured according to JIS P8117

(4) Average pore diameter: Determined by the nitrogen gas adsorption

(5) Porosity: Determined by the weight method

(6) Pin puncture strength: Determined by puncturing the sample with a pin (diameter: 1 mm, or 0.5 mm R) at 2 mm/second, to find the load at which it is broken

(7) Tensile strength and elongation at break: Determined by finding the breaking strength and elongation of a 10 mm wide rectangular sample, tested according to ASTM D822

(8) Bubble point: Determined according to ASTM E-128-61 with the sample put in ethanol. When it exceeds the upper limit, the term "No" is reported, by which is meant that it exceeds 14,700 KPa.

(9) Thermal shrinkage: Determined for both MD and TD directions, after exposing the sample to an atmosphere kept at 105°C for 8 hours

(10) Impedance: Determined by an impedance analyzer (Solartron) at 1 KHz for real part of impedance, wherein the membrane was placed between the metallic electrodes (16 mm in diameter) and immersed in an electrolytic solution. The electrolytic solution was prepared by dissolving 1 mol LiClO<sub>4</sub> in a 1:1 mixed solution of propylene carbonate and 1,2-dimethoxyethane in an argon atmosphere.

(11) Liquid retentivity: Determined by immersing the microporous membrane in an electrolytic solution dissolving 1 mol LiClO<sub>4</sub> in a 1:1 mixed solution of propylene carbonate and 1,2-dimethoxyethane, and lightly wiping the surface of the withdrawn membrane with a filter paper, where liquid retentivity is defined as quantity of the electrolytic solu-

tion held by unit mass of the membrane. The membrane having a liquid retentivity of 100% or less is judged to be insufficient in battery characteristics.

(12) Resistance to pinholing: Determined by pressing the microporous membrane with a pin (diameter: 1 mm) at a load of 1000 g for 5 seconds, to measure changed air-permeability. The membrane is judged to be insufficient in battery characteristics, when it loses 50% or more of its initial air-permeability. A sample is marked with ○ when it loses less than 50% of its initial air permeability, and with X when it loses air-permeability more.

#### EXAMPLE 1

[0046] A polyethylene mixture, comprising 30 wt.% of an ultra-high-molecular-weight polyethylene (UHMWPE) having a weight-average molecular weight of  $2.0 \times 10^6$  and 70 wt.% of a high-density polyethylene (HDPE) having a weight-average molecular weight of  $3.5 \times 10^5$ , and having a Mw/Mn ratio of 16.8 and melting point of 135°C, was incorporated with 0.375 wt. parts of an antioxidant based on 100 wt. parts of the polyethylene mixture, to prepare a polyethylene composition. Twenty (20) wt. parts of the polyethylene composition was fed to a biaxial extruder (58mm in diameter, L/D ratio = 42, high kneading type), and 80 wt. parts of liquid paraffin was also fed to the biaxial extruder from the side feeder, to prepare a polyethylene solution in the extruder by melting the polyethylene composition and kneading it with the liquid paraffin at 200°C and 200rpm. The resulting solution was extruded from the T-die attached at the extruder end in such a way to have 50 to 60 μm as thickness of the following stretched membrane, and taken up by a cooling roll, kept at 50°C, to prepare a gel-like sheet. The sheet was then biaxially stretched at 113°C at a stretching ratio of 5 in each of the MD and TD directions (5×5), to have the stretched membrane. The resulting membrane was washed with methylene chloride to remove the residual liquid paraffin by extraction, dried and heat-set at 120°C for 10 seconds to prepare a 25 μm thick microporous polyethylene membrane. The properties of the membrane are shown in Table 1.

#### EXAMPLES 2 to 11

[0047] Microporous polyethylene membranes were prepared in the same manner as in EXAMPLE 1 except that UHMWPE and HDPE were used in ratios shown in Tables 1 and 2, and stretching temperature and ratios shown in Tables 1 and 2 were used. The properties of the microporous polyethylene membranes are shown in Tables 1 and 2. All of the polyethylene compositions had a melting point of 135°C.

Table 1

| EXAMPLES                            |                          | 1     | 2                 | 3                 | 4                 | 5                 | 6                 |
|-------------------------------------|--------------------------|-------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Polyethylene compositions           | UHMWPE                   | Mw    | $2.0 \times 10^6$ | $2.0 \times 10^6$ | $2.0 \times 10^6$ | $2.0 \times 10^6$ | $2.0 \times 10^6$ |
|                                     |                          | wt%   | 30                | 30                | 40                | 40                | 40                |
|                                     | HDPE                     | Mw    | $3.5 \times 10^6$ | $3.5 \times 10^6$ | $3.5 \times 10^6$ | $3.5 \times 10^6$ | $3.5 \times 10^6$ |
|                                     |                          | wt%   | 70                | 70                | 60                | 60                | 60                |
| PE concentration in the solution    |                          | wt%   | 20                | 25                | 20                | 25                | 30                |
| Stretching conditions               | Temperature              | °C    | 113               | 113               | 114               | 114               | 114               |
|                                     | Stretching ratio         | MD×TD | 5×5               | 5×5               | 5×5               | 5×5               | 5×5               |
| Heat-setting                        | Temperature              | °C    | 120               | 120               | 120               | 120               | 120               |
|                                     | Thickness                | μm    | 25                | 25                | 25                | 25                | 25                |
| Properties of microporous membranes | Air permeability         | sec   | 365               | 408               | 449               | 421               | 435               |
|                                     | Average pore diameter    | μm    | 0.03              | 0.03              | 0.03              | 0.03              | 0.03              |
|                                     | Porosity                 | %     | 44.8              | 45.6              | 45                | 45.5              | 45.5              |
|                                     | Pin puncture strength    | mN    | 5220              | 5770              | 6070              | 5360              | 5840              |
|                                     | Tensile strength (MD)    | Kpa   | 101100            | 111100            | 110100            | 108300            | 114200            |
|                                     | Tensile strength (TD)    |       | 83500             | 82400             | 82400             | 87100             | 90600             |
|                                     | Elongation at break (MD) | %     | 314               | 306               | 306               | 324               | 314               |
|                                     | Elongation at break (TD) |       | 481               | 374               | 374               | 496               | 428               |
|                                     | Bubble point             | Kpa   | No                | No                | No                | No                | No                |
|                                     | Thermal shrinkage (MD)   | %     | 7.5               | 9                 | 9                 | 8                 | 8.5               |
|                                     | Thermal shrinkage (TD)   |       | 4.5               | 6.5               | 6.5               | 5                 | 6.5               |
|                                     | Impedance                | Ω/cm² | 2.6               | 2.3               | 2.8               | 2.7               | 2.7               |
|                                     | Liquid retentivity       | %     | 120               | 110               | 105               | 110               | 110               |
|                                     | Resistance to pinholing  | —     | ○                 | ○                 | ○                 | ○                 | ○                 |



Table 2

| EXAMPLES                            |                       |      | 7                 | 8                   | 9                   | 10                  | 11                  |                     |
|-------------------------------------|-----------------------|------|-------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Polyethylene compositions           | UHMWPE                |      | Mw                | 2.0×10 <sup>6</sup> | 2.0×10 <sup>6</sup> | 2.0×10 <sup>6</sup> | 2.0×10 <sup>6</sup> | 2.0×10 <sup>6</sup> |
|                                     |                       |      | wt%               | 50                  | 30                  | 30                  | 30                  | 40                  |
|                                     | HDPE                  |      | Mw                | 3.5×10 <sup>5</sup> | 3.5×10 <sup>5</sup> | 3.5×10 <sup>5</sup> | 3.5×10 <sup>5</sup> | 3.5×10 <sup>5</sup> |
|                                     |                       |      | wt%               | 50                  | 70                  | 70                  | 70                  | 60                  |
| PE concentration in the solution    |                       |      | wt%               | 20                  | 20                  | 30                  | 20                  | 20                  |
| Stretching conditions               | Temperature           |      | °C                | 113                 | 113                 | 113                 | 120                 | 120                 |
|                                     | Stretching ratio      |      | MD×TD             | 5×5                 | 5×5                 | 5×5                 | 7×7                 | 7×7                 |
| Heat-setting                        | Temperature           |      | °C                | 125                 | 125                 | 125                 | 120                 | 120                 |
| Properties of microporous membranes | Thickness             |      | μm                | 25                  | 25                  | 25                  | 25                  | 25                  |
|                                     | Air permeability      |      | sec               | 601                 | 589                 | 653                 | 786                 | 774                 |
|                                     | Average pore diameter |      | μm                | 0.032               | 0.033               | 0.03                | 0.025               | 0.026               |
|                                     | Porosity              |      | %                 | 38                  | 37.7                | 37.5                | 47.7                | 48.2                |
|                                     | Pin puncture strength |      | mN                | 8180                | 7200                | 7890                | 8670                | 8890                |
|                                     | Tensile strength      | (MD) | Kpa               | 165100              | 155800              | 161700              | 166100              | 166800              |
|                                     |                       | (TD) |                   | 130000              | 127400              | 132300              | 141600              | 140700              |
|                                     | Elongation at break   | (MD) | %                 | 332                 | 388                 | 302                 | 305                 | 344                 |
|                                     |                       | (TD) |                   | 389                 | 421                 | 355                 | 388                 | 395                 |
|                                     | Bubble point          |      | Kpa               | No                  | No                  | No                  | No                  | No                  |
|                                     | Thermal shrinkage     | (MD) | %                 | 6.6                 | 4.8                 | 5.8                 | 8                   | 8.2                 |
|                                     |                       | (TD) |                   | 5.1                 | 4.1                 | 4.4                 | 6.9                 | 6.8                 |
|                                     | Impedance             |      | Ω/cm <sup>2</sup> | 2.9                 | 2.9                 | 3                   | 3.2                 | 3.1                 |
|                                     | Liquid retentivity    |      | %                 | 105                 | 110                 | 105                 | 100                 | 100                 |
| Resistance to pinholing             |                       | -    | ○                 | ○                   | ○                   | ○                   | ○                   |                     |

## COMPARATIVE EXAMPLES 1 to 5

[0048] Microporous polyethylene membranes were prepared in the same manner as in EXAMPLE 1 except that UHMWPE and HDPE were used in ratios shown in Tables 1 and 2, and stretching temperature and ratios shown in Tables 1 and 2 were used. The properties of the membranes are shown in Table 3. All of the polyethylene compositions had a melting point of 135°C.

Table 3

| COMPARATIVE EXAMPLES            |        |     | 1                   | 2                   | 3                   | 4                   | 5                   |
|---------------------------------|--------|-----|---------------------|---------------------|---------------------|---------------------|---------------------|
| Polyethylene compositions       | UHMWPE | Mw  | 2.0×10 <sup>6</sup> | 2.0×10 <sup>6</sup> | 2.0×10 <sup>6</sup> | 2.0×10 <sup>6</sup> | 2.0×10 <sup>6</sup> |
|                                 |        | wt% | 20                  | 18                  | 5                   | 30                  | 30                  |
|                                 | HDPE   | Mw  | 3.5×10 <sup>5</sup> | 5.0×10 <sup>4</sup> | 5.0×10 <sup>4</sup> | 3.5×10 <sup>5</sup> | 3.5×10 <sup>5</sup> |
|                                 |        | wt% | 80                  | 82                  | 95                  | 70                  | 70                  |
| PE concentratin in the solution |        | wt% | 30                  | 30                  | 30                  | 20                  | 25                  |

Table 3 (continued)

| COMPARATIVE EXAMPLES                |                       |                   | 1     | 2      | 3      | 4     | 5     |       |
|-------------------------------------|-----------------------|-------------------|-------|--------|--------|-------|-------|-------|
| Stretching conditions               | Temperature           |                   | °C    | 117    | 114    | 118   | 120   | 118   |
|                                     | Stretching ratio      |                   | MD×TD | 5×5    | 5×5    | 5×5   | 3×3   | 4×4   |
| Heat-setting                        | Temperature           |                   | °C    | 125    | 120    | 122   | 120   | 120   |
| Properties of microporous membranes | Thickness             |                   | μm    | 25     | 25     | 25    | 25    | 25    |
|                                     | Air permeability      |                   | sec   | 955    | 621    | 650   | 199   | 275   |
|                                     | Average pore diameter |                   | μm    | 0.03   | 0.03   | 0.035 | 0.045 | 0.039 |
|                                     | Porosity              |                   | %     | 31     | 45     | 40    | 51    | 48.8  |
|                                     | Pin puncture strength |                   | mN    | 6080   | 4410   | 4210  | 2170  | 2910  |
|                                     | Tensile strength      | (MD)              | Kpa   | 117600 | 100900 | 96000 | 58900 | 67000 |
|                                     |                       | (TD)              |       | 103400 | 83800  | 76900 | 44700 | 46800 |
|                                     | Elongation at break   | (MD)              | %     | 210    | 300    | 180   | 441   | 412   |
|                                     |                       | (TD)              |       | 412    | 450    | 290   | 912   | 788   |
|                                     | Bubble point          |                   | Kpa   | No     | No     | No    | No    | No    |
|                                     | Thermal shrinkage     | (MD)              | %     | 5      | 7      | 5     | 3.2   | 3.6   |
|                                     |                       | (TD)              |       | 3      | 4.5    | 3.6   | 0.9   | 1.9   |
| Impedance                           |                       | Ω/cm <sup>2</sup> | 4     | 2.8    | 2.7    | 2.8   | 2.4   |       |
| Liquid retentivity                  |                       | %                 | 70    | 105    | 105    | 130   | 125   |       |
| Resistance to pinholing             |                       | -                 | ○     | X      | X      | X     | X     |       |

## INDUSTRIAL APPLICABILITY

[0049] As described in detail, the microporous polyolefin membrane of the present invention comprises an ultra-high-molecular-weight polyolefin or composition containing an ultra-high-molecular-weight polyolefin, and is high in pin puncture strength, adequate in pore diameter and high in porosity (permeability), and, when used for battery separators, shows excellent battery characteristics and high safety characteristics. These properties make the membrane of the present invention suitable for, e.g., battery separators and liquid filters.

## Claims

1. A microporous polyolefin membrane, comprising (A) an ultra-high-molecular-weight polyolefin having a weight-average molecular weight of  $5 \times 10^5$  or more, or (B) a composition containing an ultra-high-molecular-weight polyolefin having a weight-average molecular weight of  $5 \times 10^5$  or more, and having a porosity of 30 to 95%, bubble point exceeding 980 KPa and pin puncture strength of 4,900 mN/25 μm or more.
2. The microporous polyolefin membrane according to Claim 1, wherein said ultra-high-molecular-weight polyolefin (A) having a weight-average molecular weight of  $5 \times 10^5$  or more is polyethylene or polypropylene.
3. The microporous polyolefin membrane according to Claim 1 or 2, wherein said composition (B) containing an ultra-high-molecular-weight polyolefin having a weight-average molecular weight of  $5 \times 10^5$  or more comprises an ultra-high-molecular-weight polyolefin (B-1) having a weight-average molecular weight of  $1 \times 10^6$  or more and high-density polyolefin (B-2) having a weight-average molecular weight of  $1 \times 10^5$  or more but less than  $5 \times 10^5$ .
4. The microporous polyolefin membrane according to one of Claims 1 to 3, which has an average pore diameter of 0.01 to 0.1 μm.
5. The microporous polyolefin membrane according to one of Claims 1 to 4, which has a porosity of 45 to 95%.

6. The microporous polyolefin membrane according to one of Claims 1 to 5, which has a tensile elongation of 300% or more.
7. The microporous polyolefin membrane according to one of Claims 1 to 6, which has a pin puncture strength of 6,860 mN/25  $\mu$ m or more and tensile strength of 127,400 KPa or more.
8. The microporous polyolefin membrane according to one of Claims 1 to 7, which has an air-permeability of 900 sec/100 cc or less.
9. The microporous polyolefin membrane according to one of Claims 1 to 8, which has a thermal shrinkage of 10% or less both in the MD and TD directions.
10. The microporous polyolefin membrane according to one of Claims 1 to 9, which loses less than 50% of the initial air-permeability, when pressed with a pin having a diameter of 1 mm at a load of 1000 g for 5 seconds.
11. A method for producing the microporous polyolefin membrane of Claim 1, which comprises the steps of (a) preparing a solution comprising 10 to 40 wt. % of (A) an ultra-high-molecular-weight polyolefin having a weight-average molecular weight of  $5 \times 10^5$  or more, or (B) a composition containing an ultra-high-molecular-weight polyolefin having a weight-average molecular weight of  $5 \times 10^5$  or more, and 90 to 60 wt.% of a solvent, (b) extruding the solution, (c) quenching the extruded solution to have a gel-like extrudate, (d) biaxially stretching the gel-like extrudate at 110 to 120°C at a stretching ratio of 5 or more in both MD and TD directions, (e) removing the solvent and drying the extrudate, and (f) heat-setting the extrudate at 115 to 125°C.
12. The method for producing the microporous polyolefin membrane according to Claim 11, wherein said composition (B) containing an ultra-high-molecular-weight polyolefin having a weight-average molecular weight of  $5 \times 10^5$  or more comprises 20 to 60 wt.% of an ultra-high-molecular-weight polyethylene (B-1) having a weight-average molecular weight of  $1 \times 10^6$  or more and 40 to 80 wt.% of a high-density polyethylene (B-2) having a weight-average molecular weight of  $1 \times 10^5$  or more but less than  $5 \times 10^5$ .
13. The method for producing the microporous polyolefin membrane according to Claim 11 or 12, wherein said gel-like extrudate is stretched at 113 to 120°C.
14. A battery separator which uses the microporous polyolefin membrane according to Claim 1.
15. A battery which uses the microporous polyolefin membrane according to Claim 1 for the battery separator.
16. A filter which uses the microporous polyolefin membrane according to Claim 1.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/00830

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.<sup>7</sup>

C08J9/00, H01M2/16, B01D71/26

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.<sup>7</sup>

C08J9/00, H01M2/16, B01D71/26

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                           | Relevant to claim No. |
|-----------|--|-----------------------|
| X         | JP, 9-104775, A (TONEN CHEMICAL CORP.),  | 1-15                  |
| A         | 22 April, 1997 (22.04.97),<br>Claims; Par. Nos. [0030], [0033] to [0038] (Family: none)                      | 16                    |
| A         | JP, 11-21361, A (Mitsubishi Chemical Corporation),<br>26 January, 1999 (26.01.99),<br>Claims (Family: none)  | 1-16                  |
| A         | JP, 9-220453, A (Asahi Chemical Industry Co., Ltd.),<br>26 August, 1997 (26.08.97),<br>Claims (Family: none) | 1-16                  |

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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Date of the actual completion of the international search  
26 April, 2000 (26.04.00)Date of mailing of the international search report  
16.05.00Name and mailing address of the ISA/  
Japanese Patent Office

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